KU LEUVEN

ISGC 2017
May 16^{th} - 19^{th}

Liquid Cobalt Salts as Non-Volatile Electrolytes for High Current Density Electrodeposition of Cobalt and Electrochemical Synthesis of Cobalt Nanoparticles

PIETER GEYSENS
Jeroen Sniekers
Jan Fransaer
Koen Binnemans

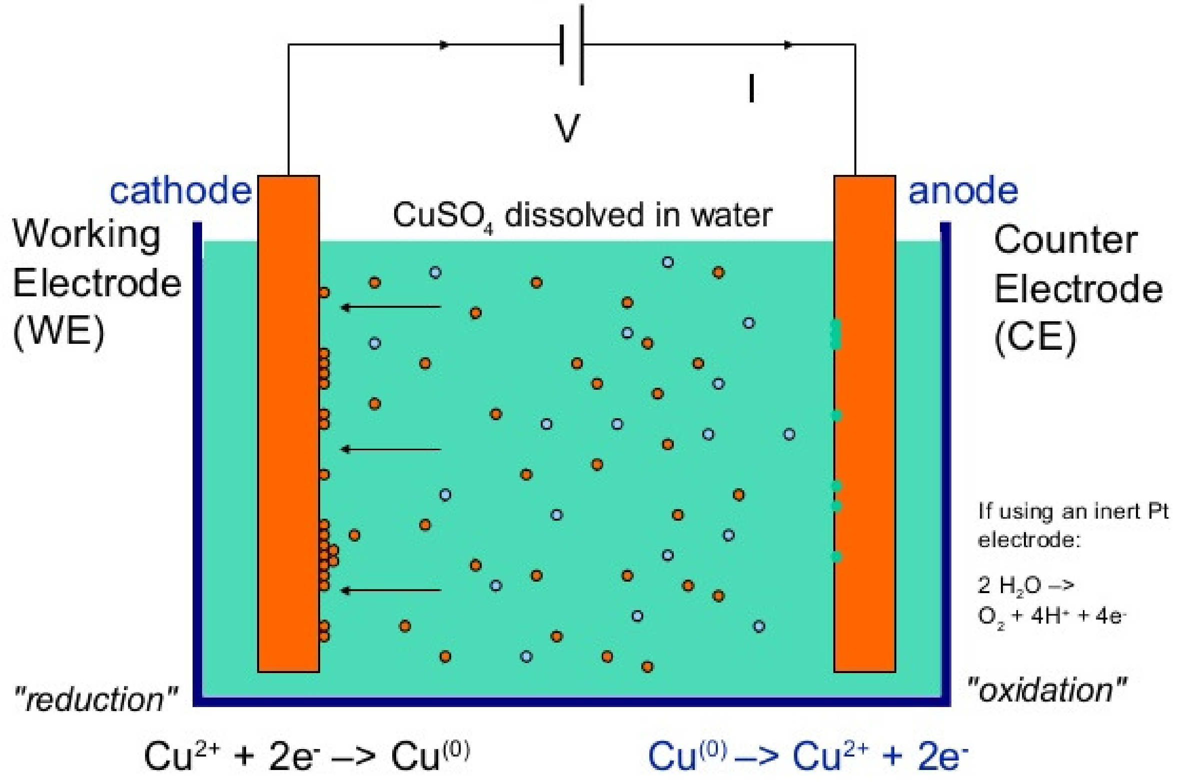
Laboratory of inorganic chemistry (LIC)
KULeuven

Overview

- Introduction
  - Electrodeposition
  - Liquid metal salts (LMS)
- Previous work on LMS
- Results
  - Synthesis of cobalt(II)-containing LMS
  - Characterization
  - Electrodeposition from $[Co(DMAc)_6][Tf_2N]_2$
  - Electrodeposition from $[Co(HeIm)_6][Tf_2N]_2$
  - Proposed mechanism nanoparticle formation
- Conclusions

Electrodeposition

- Definition: reduction of metal ions in solution under influence of a negative potential to form metallic deposits on the cathode.
  - Electroplating: coating of conductive surfaces with metallic layers by electrodeposition.



KU LEUVEN

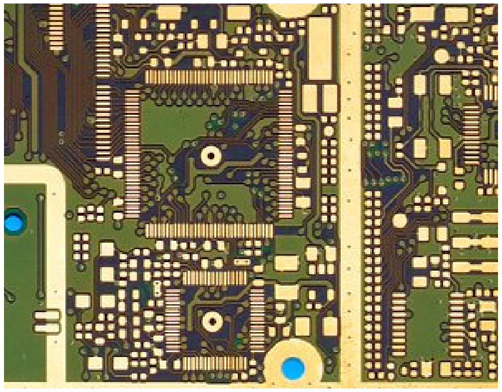
Electrodeposition

- Applications

Galvanized steel (Zn)

Silver plated tea sets

Chrome plating



Circuit boards (Cu)

Nickel/cobalt plating

KU LEUVEN

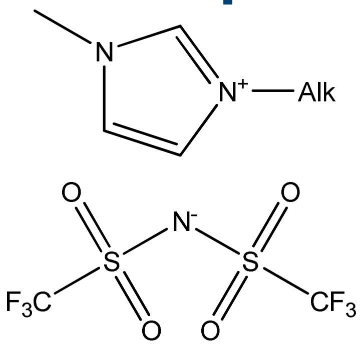
Aqueous electrolytes

- Water has a narrow electrochemical window (1.23 V)
- Aqueous electroplating solutions often contain hazardous chemicals
  - Highly acidic Cr(VI) electrolytes for chrome plating (carcinogen)
  - Boric acid for nickel plating (reproductive toxin)
  - Cyanide as complexing agent for copper, silver and gold plating

→ Alternative electrolytes necessary

Liquid metal salts (LMS)

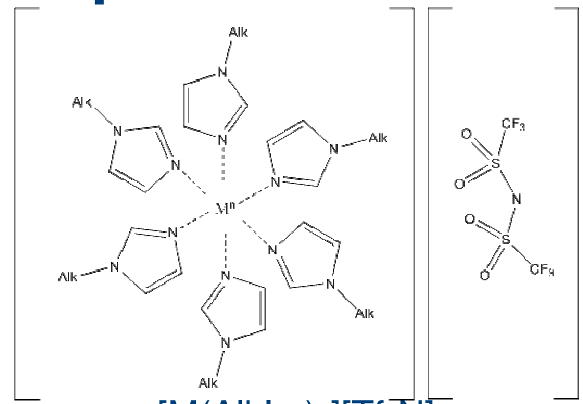
Ionic liquids



$[C_nmim][Tf_2N]$

+ Inherent conductivity
+ Wide electrochemical window
+ Wide liquidus range
+ High thermal stability
+ Negligible volatility
– Poor solvents for metal salts
– High viscosity

Liquid metal salts

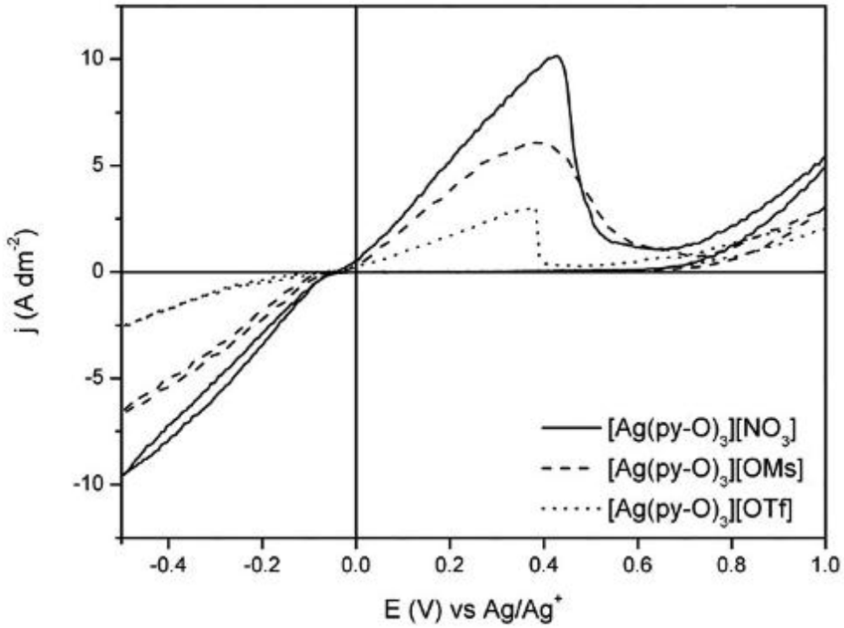


$[M(AlkIm)_6][Tf_2N]_n$

+ Inherent conductivity
+ Wide electrochemical window
+ Wide liquidus range
+ High thermal stability
+ Negligible volatility
+ Metal ion integrated in IL structure
  → very high metal concentration

Previous work on LMS

- High current density silver electroplating from $[Ag(Py\text{-}O)_3][NO_3]$



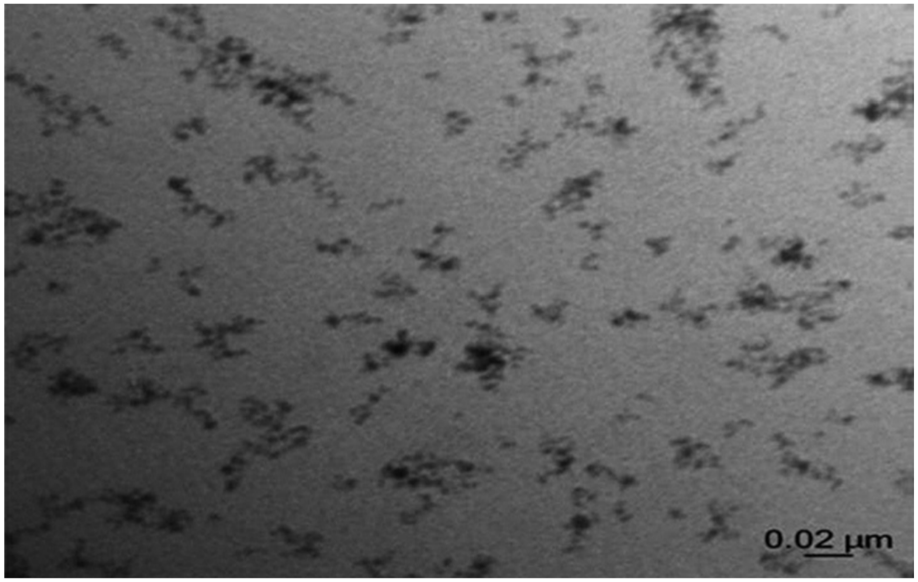
Sniekers et al., *Dalton Trans.*, 2014, **43**, 1589–1598.

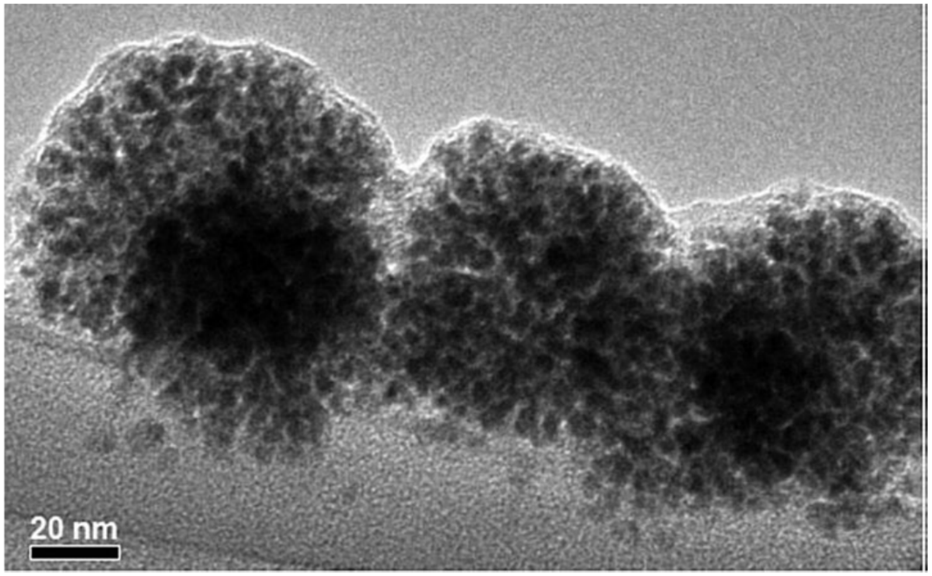
- Other successfully deposited metals:
  - Copper from $[Cu(MeCN)_4][Tf_2N]$ Schaltin et al. *J.Electrochem. Soc.*, 2011, **158**, D21–D27.
  - Palladium from $[Pd(AlkIm)_4][Tf_2N]_2$ Schaltin et al. *Chem. Commun.*, 2014, **50**, 10248–10250.
  - Zinc from $[Zn(AlkIm)_4][Tf_2N]_2$ Steichen et al. *Dalton Trans.*, 2014, **43**, 12329–12341.

KU LEUVEN

Previous work on LMS

- Electrochemical nanoparticle formation from $[Mn(AlkIm)_6][Tf_2N]_2$ and $[Ni(AlkIm)_6][Tf_2N]_2$





Sniekers et al. *Chem. Eur. J.*, 2016, **22**, 1010–1020.

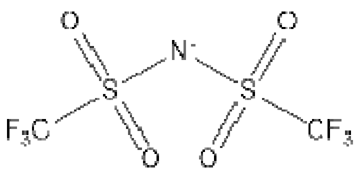
Sniekers et al, *Dalton Trans.*, 2017, **46**, 2497–2509.

Synthesis of Co(II)-containing LMS

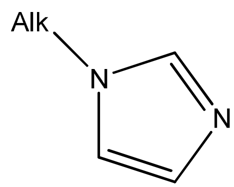
1. $CoCO_3 \cdot xH_2O + 2\ HX \rightarrow [Co(H_2O)_6][X]_2 + y\ H_2O + CO_2$

   $X = Tf_2N^-, OMs^-$

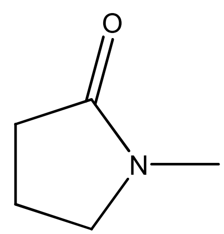
2. $[Co(H_2O)_6][X]_2 + 6\ L \rightarrow [Co(L)_6][X]_2 + 6\ H_2O$



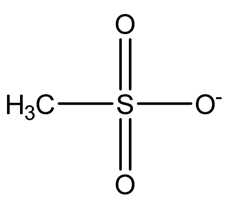
Bis(trifluoromethylsulfonyl)imide (Tf_2N)



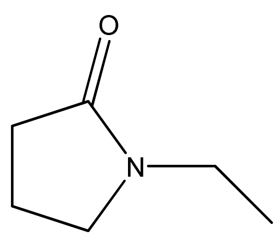
N-alkylimidazole (AlkIm)



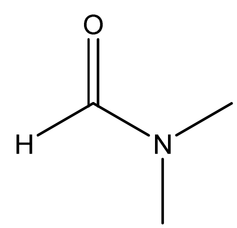
N-methylpyrrolidone (NMP)



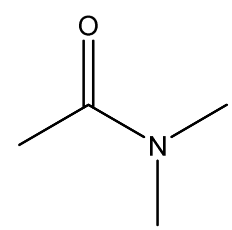
methanesulfonate (OMs)



N-ethylpyrrolidone (NEP)



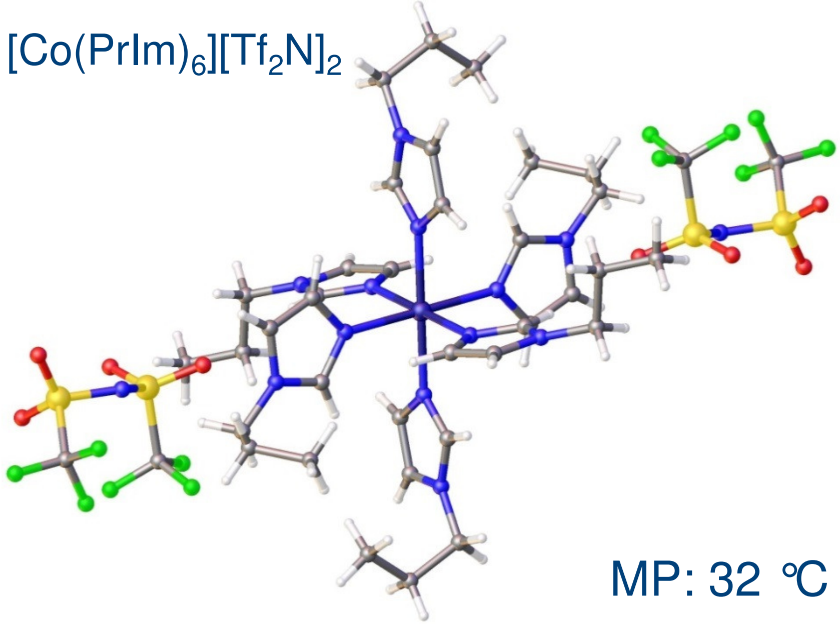
*N,N-di*methylformamide (DMF)



*N,N-di*methylacetamide (DMAc)

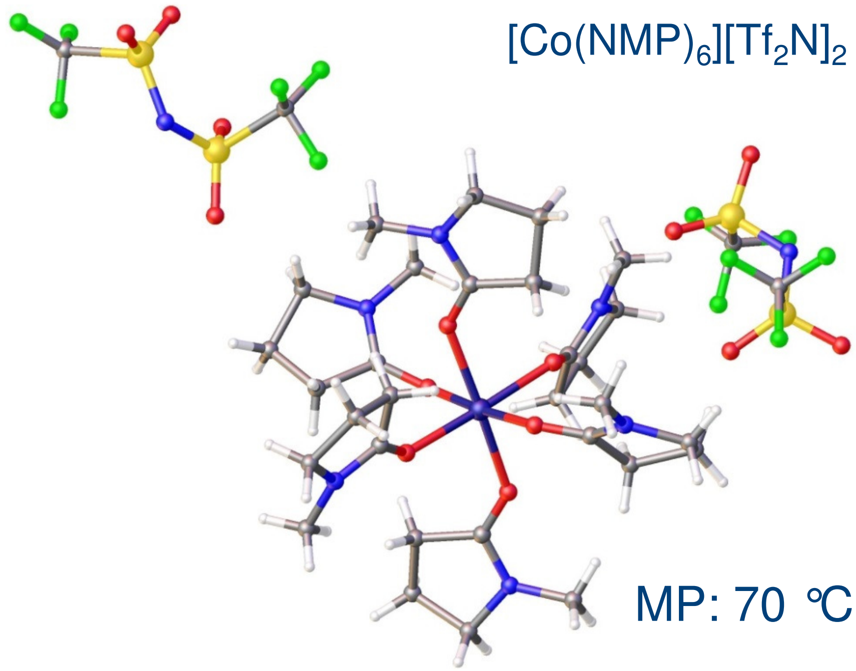
Results: crystal structures

$[Co(PrIm)_6][Tf_2N]_2$

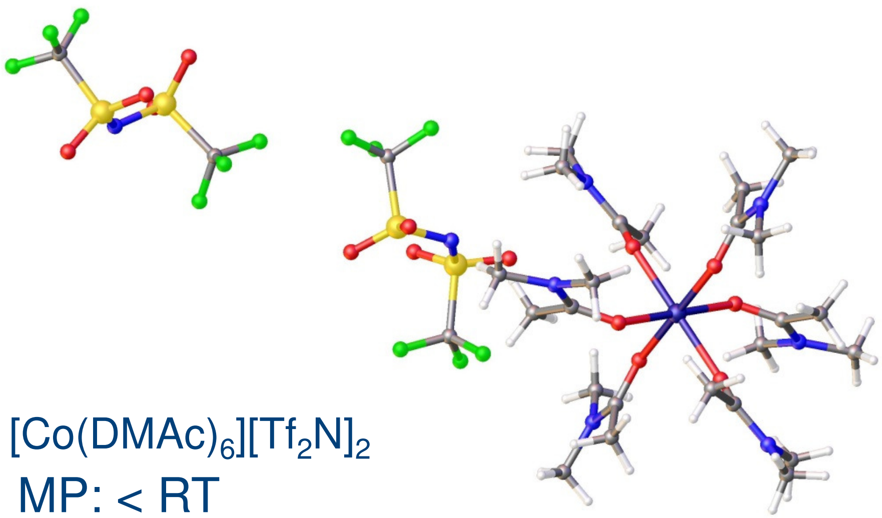


MP: 32 °C

$[Co(NMP)_6][Tf_2N]_2$

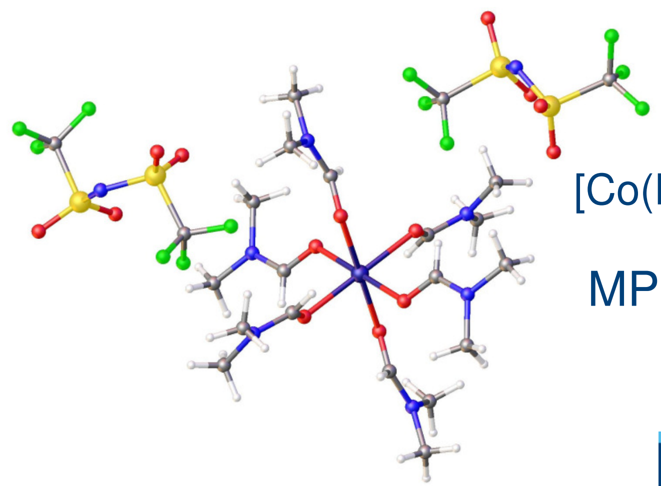


MP: 70 °C



$[Co(DMAc)_6][Tf_2N]_2$

MP: < RT

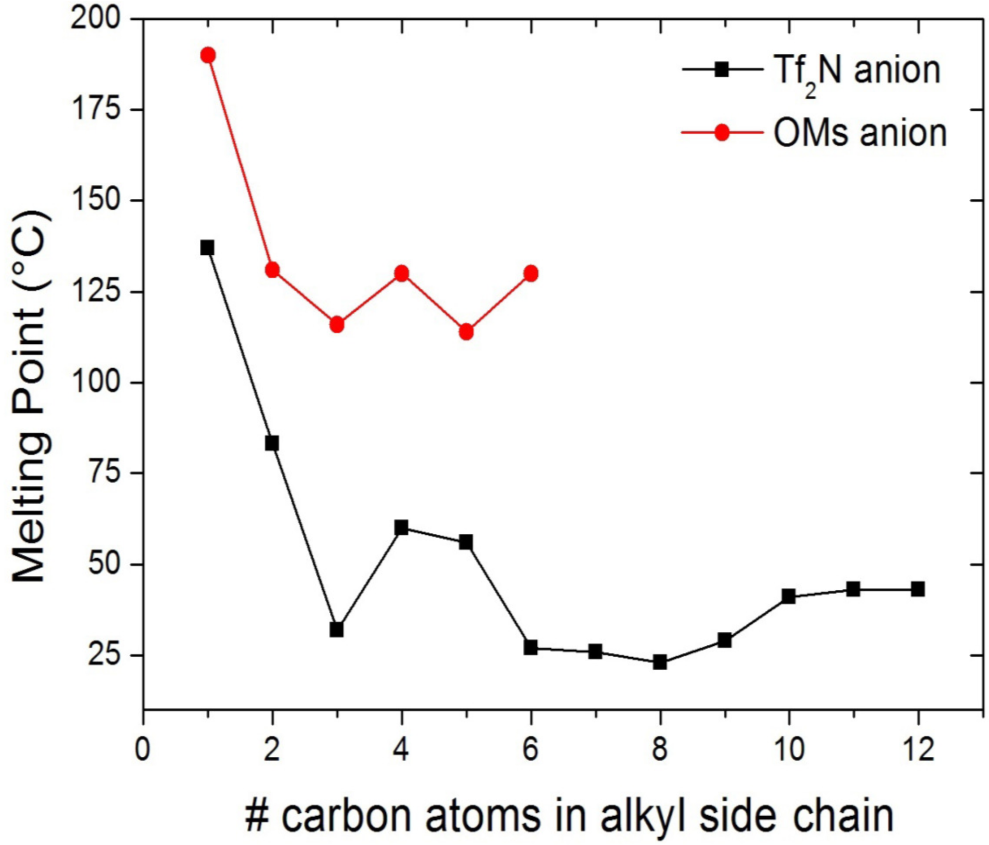


$[Co(DMF)_6][Tf_2N]_2$

MP: 104 °C

KU LEUVEN

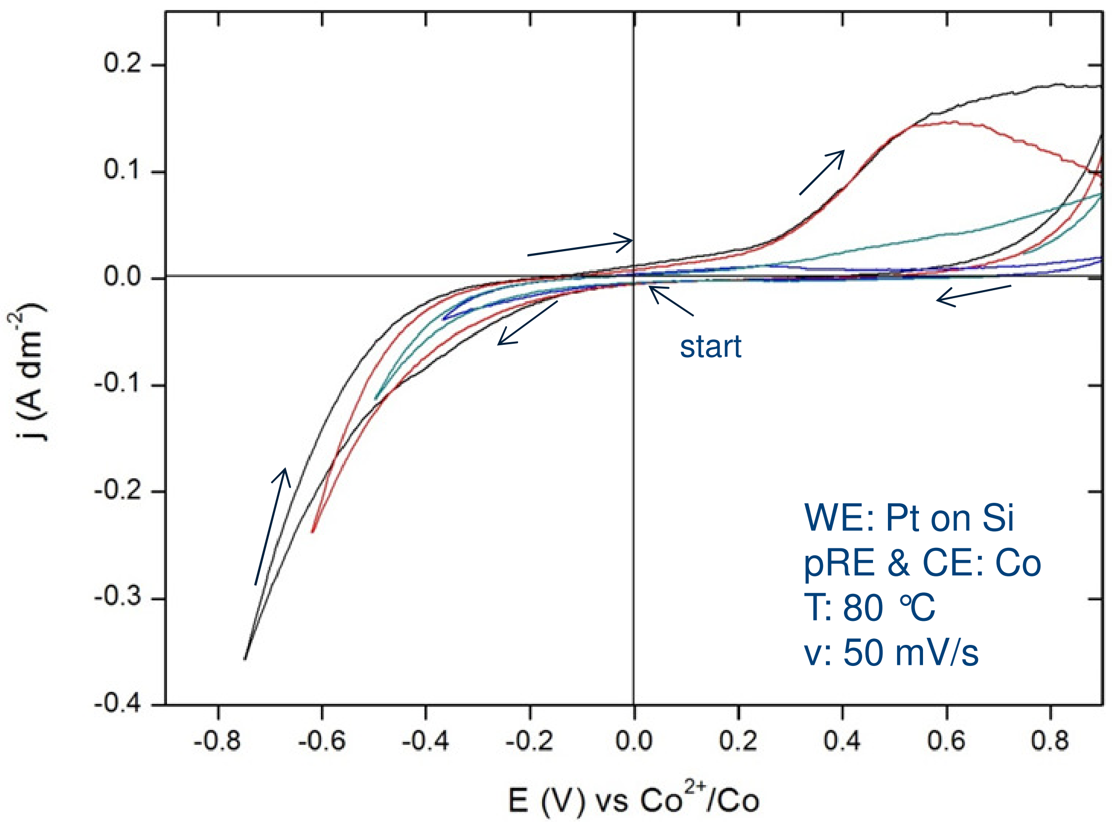
Melting points of the $[Co(AlkIm)_6][Tf_2N]_2$ series



- Minimum for octyl side chain
- Odd/even effect

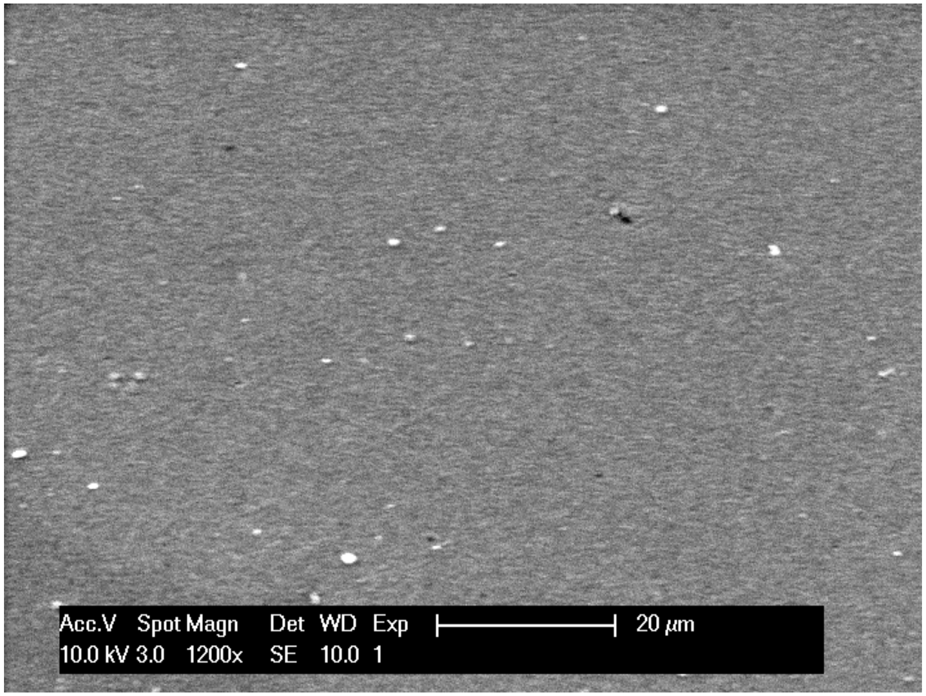
KU LEUVEN

Electrodeposition from $[Co(DMAc)_6][Tf_2N]_2$

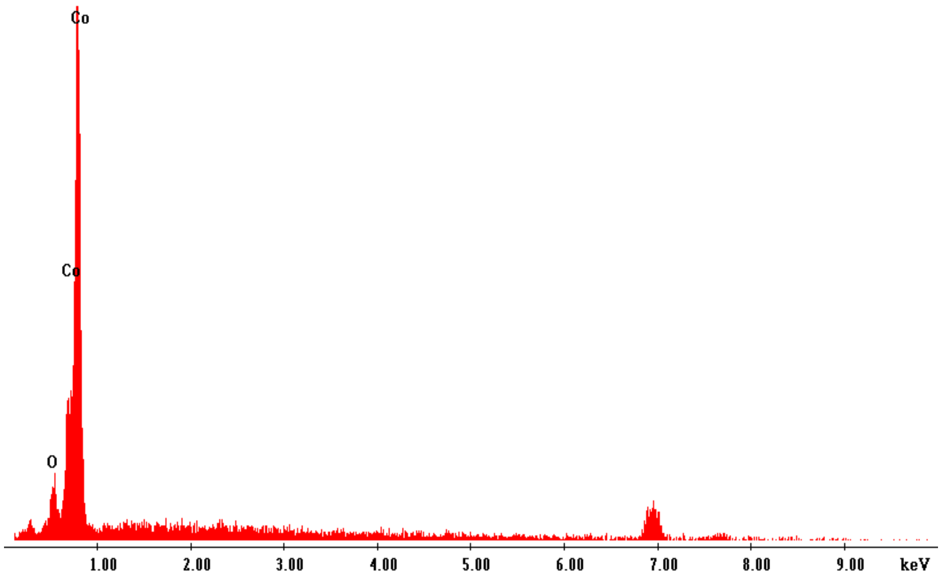


- High deposition current density possible
- No limiting current for cobalt electrodeposition
- Co deposition/stripping is reversible

Electrodeposition from $[Co(DMAc)_6][Tf_2N]_2$

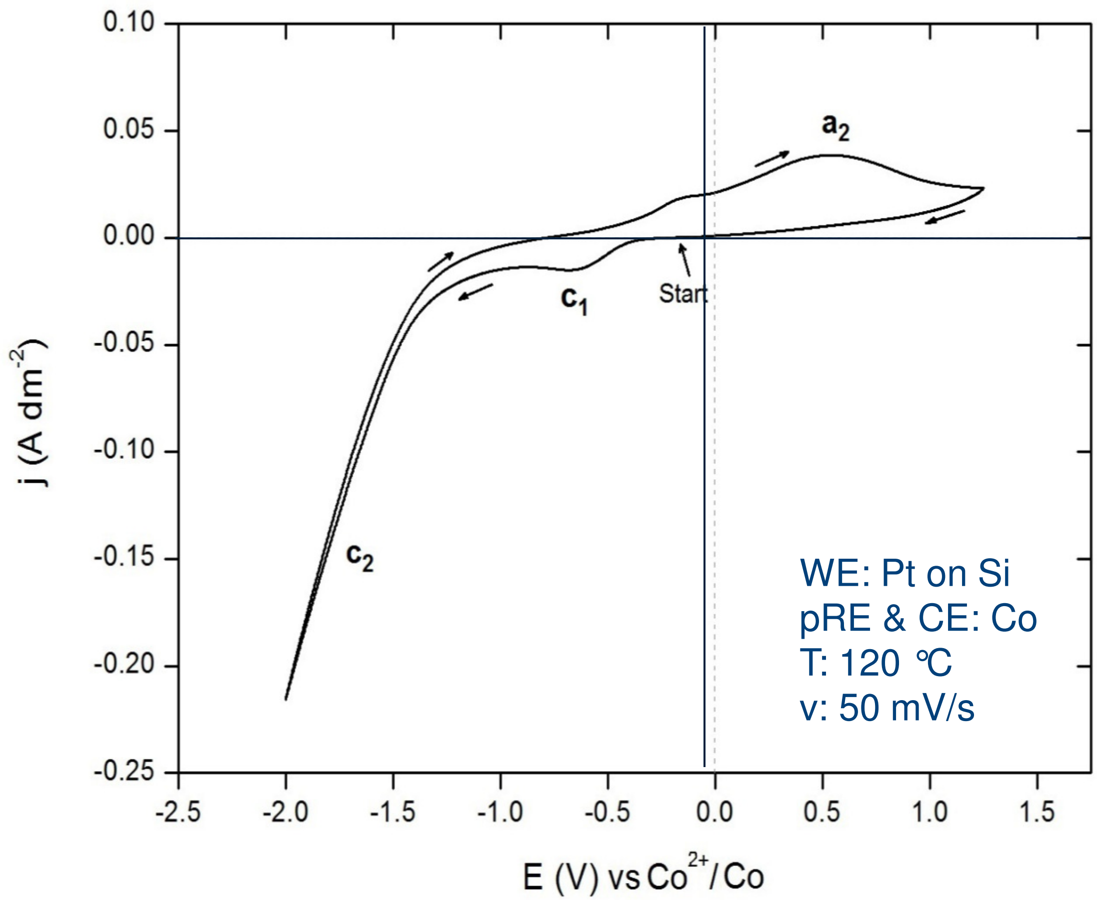


Theoretical thickness deposit = 1.8 µm



- Thick, smooth and uniform nodular cobalt depositions were obtained from $Co(DMAc)_6][Tf_2N]_2$ and LMS with other amide ligands

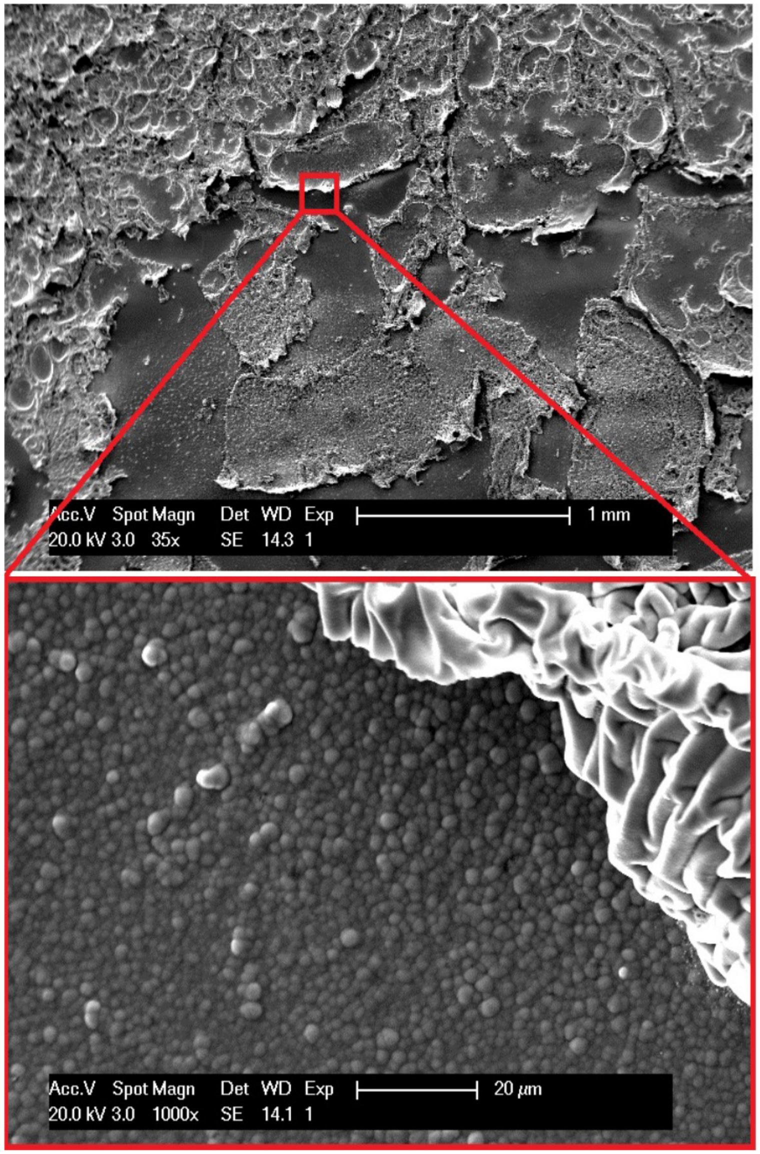
Electrodeposition from $[Co(HeIm)_6][Tf_2N]_2$



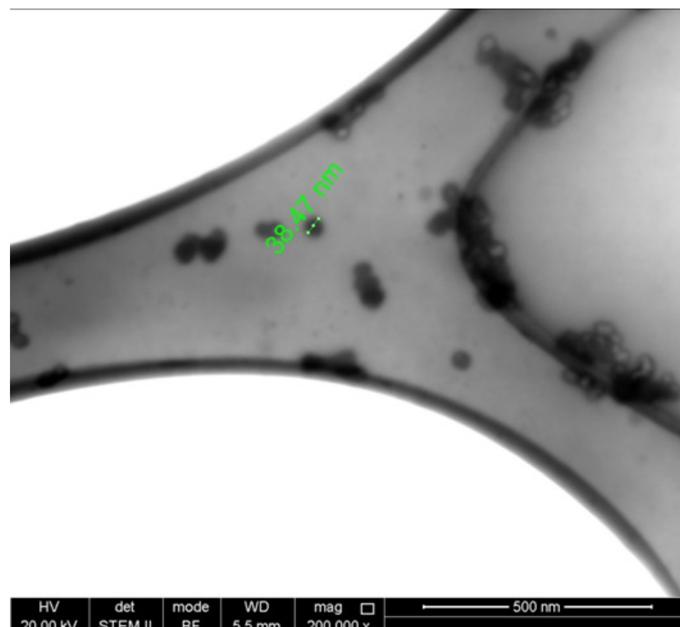
- Small cathodic peak c_1 → reduction AlkIm ligand
- Large overpotential for cobalt deposition
- Poor reversibility for Co deposition/stripping
- Black discoloration around cathode

KU LEUVEN

Electrodeposition from $[Co(HeIm)_6][Tf_2N]_2$

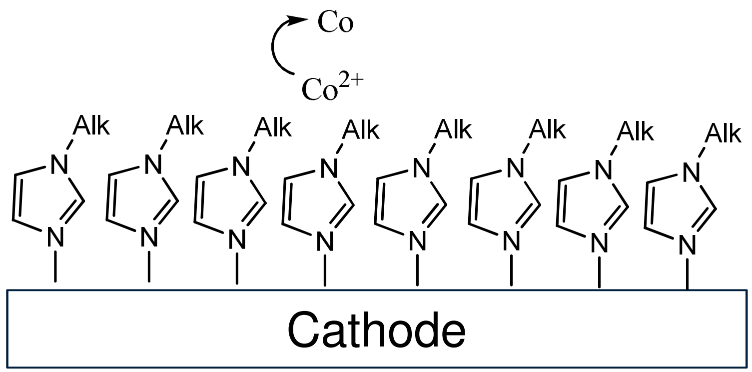


- Flaky depositions with underneath monodisperse nanoparticles
- Nanoparticles also found dispersed in electrolyte
- Similar behavior for other AlkIm LMS of Co, Mn and Ni



Proposed mechanism NP formation

- *N*-alkylimidazoles adsorb on cathode to form blocking layer
- Electrons have to tunnel through this layer
- Co(II) is reduced at a distance from the cathode to single Co(0) atoms
- Due to high surface energy, single Co(0) atoms recombine into poor adhesive deposits and nanoparticles
- *N*-alkylimidazoles behave as surfactants to stabilize NPs so they diffuse in the electrolyte



KU LEUVEN

Conclusions

- Cobalt liquid metal salts are non-volatile alternatives for cobalt electrodeposition at high current density
- Deposition morphology can be tuned by choice of ligands
  - Amide ligands enable deposition of thick crack-free layers
  - *N*-alkylimidazoles enable formation of nanoparticles
- LMS strategy can be applied to many metals

Aknowledgements

Koen Binnemans
Jan Fransaer
Jeroen Sniekers
Luc van Meervelt (XRD)
LIC collegues
ISGC organization

Thank you for your attention

KU LEUVEN